

Microstructures and liquid phase separation in multicomponent CoCrCuFeNi high entropy alloys

P. H. Wu¹, N. Liu^{*1}, P. J. Zhou¹, Z. Peng¹, W. D. Du¹, X. J. Wang^{*1} and Y. Pan²

The microstructures of high entropy alloys of the system CoCrCuFe_xNi and CoCrCuFeNi_x (where x indicates the molar ratio, which, where not specified, is 1) have been investigated. Many Cu rich spheres were evident in the microstructure of CoCrCuFe_{0.5}Ni and CoCrCuFeNi_{0.5} alloys, which indicates that liquid phase separation had occurred before solidification. During liquid phase separation, the original liquids separated into two liquids: Cu rich and Cu depleted. In contrast, in other alloys ($x = 1.0, 1.5$ and 2.0), typical dendritic and interdendritic structures are obtained. Cu and/or Cr rich precipitates, with various morphologies, can be seen in the interdendritic region. Additionally, Cu rich nanoparticles and Cr rich bird shaped structures can be observed in the Cu rich spheres. Sluggish cooperative diffusion causes the element segregation and formation of nanoprecipitates in the microstructures. The calculated positive mixing enthalpies of CoCrCuFe_{0.5}Ni and CoCrCuFeNi_{0.5} alloys are likely reasons for their liquid phase separation.

Keywords: High entropy alloys, Microstructure, Nanoprecipitates, Liquid phase separation

Introduction

High entropy alloy,¹ also defined as multicomponent alloy,² is a new class of metallic material featuring more than five principal elements. The previous studies have shown that high entropy alloys consist of simple solid solution structures [face centred cubic (FCC), body centred cubic (BCC) or FCC + BCC]. Moreover, high entropy alloys show promising properties, including high temperature stability, mechanical properties and corrosion resistance. First reported by Cantor *et al.*, FCC structured FeNiCoCrMn equiatomic alloy² was studied extensively by Wu *et al.*^{3–5} recently, including the recovery, recrystallisation, grain growth and phase stability of quaternary, ternary and binary equiatomic alloys made from constituent elements of FeNiCoCrMn alloy.³ Moreover, the tensile tests were performed at temperatures in the range of 77–263 K, which showed that the yield and ultimate strengths of equiatomic FeNiCoCrMn alloy increased as the temperature decreased.^{4,5} In another widely investigated AlCoCrCuFeNi system alloys, the ordered FCC nanoparticles were found in Al_{0.5}CoCrCuFeNi and Cu free Al_{0.3}CoCrFeNi alloys.^{6,7} In addition, sunflower-like microstructure was obtained in a Co free Al₂CrCuFeNi₂⁸ high entropy alloy, the petals were $\sim 1.4 \mu\text{m}$ in length and 300

nm in width, and the seeds had an average size of 230 nm. Al element was reported to promote the transformation from FCC to BCC phase, and the hardness of Al_xCoCrCuFeNi alloys increased with Al content, but significant increase of hardness was seen only when $x > 1.0$.^{6,9} Moreover, microstructural features and micromechanical behaviour of Al_{0.8}CoCrCuFeNi HEA had been determined.¹⁰

A special liquid phase separation occurs in some monotectic alloys, because a temperature range exists where the system is in the two-phase liquid region according to the phase diagram, which is called a miscibility gap.¹¹ The immiscible therefore has also a wide range of applications. Metallic monotectic systems are mostly used as bearings (Cu–Sn–Pb) in car engines, electrical contacts and switches (Ni–Ag). The liquid immiscible alloys have been studied extensively and reviewed by Ratke and Diefenbach.¹¹ A miscibility gap in the liquid state can also be found in some ternary alloy systems containing Cu element, such as Mo–Fe–Cu, Mo–Ni–Cu, Cr–Fe–Cu, Cr–Mo–Cu and Cr–Ni–Cu alloys.¹² Liquid phase separation in multicomponent high entropy alloys, however, has not been reported until our recent research in CoCrCu_xFeMoNi high entropy alloys.¹³

Previously, the effects of aging and annealing treatment on the microstructure and properties of Cu_{0.5}CoCrFeNi high entropy alloys have been investigated.^{14,15} However, studies on the as cast microstructure and solidification procedure of CoCrCuFeNi system high entropy alloys are still absent. So, in this present work, the relative content of Fe and Ni elements is changed to deeply understand the effects of

¹School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, Jiangsu 212003, China

²Xi'an Thermal Power Research Institute Co. Ltd, Xi'an, Shaanxi 710032, China

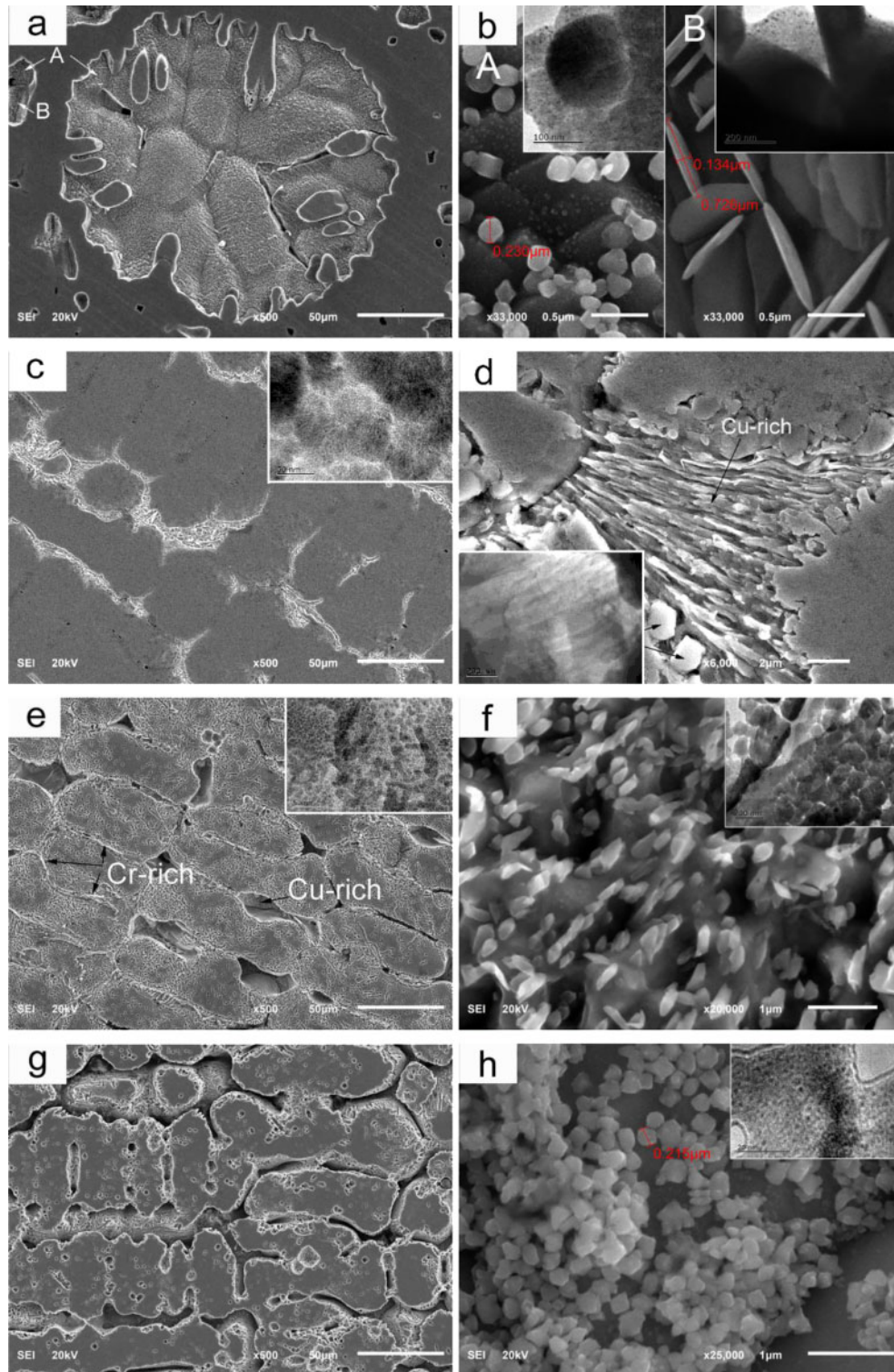
*Corresponding author, email liuning-mary@163.com (N.L.), xjwang.0@163.com (X.J.W.).

Fe and Ni contents on the microstructure of CoCrCu-FeNi system high entropy alloys.

Experimental

CoCrCuFe_xNi and CoCrCuFeNi_x alloys (x values in molar ratio, $x = 0.5, 1.0, 1.5$ and 2.0) were prepared in a quartz crucible with suitable amounts of pure elements of purity better than 99.9 wt-%. Subscripts in the alloy compositions indicate the atomic portion of individual

element. The mixtures of constituent elements were melted in a high frequency induction coil. The surface of the sample was covered by little amount of borate glass so as to prevent the contact between alloy and the atmosphere and to dissolve metal oxides and other impurities. The as solidified specimens were sectioned and polished, and then etched with chloroazotic acid. The microstructures of each specimen were examined using scanning electron microscope (SEM, JEOL JSM-6480) equipped with energy dispersive spectrometry



a, b $x = 0.5$; c, d $x = 1.0$; e, f $x = 1.5$; g, h $x = 2.0$

1 Microstructures and nanostructures of CoCrCuFe_xNi high entropy alloys

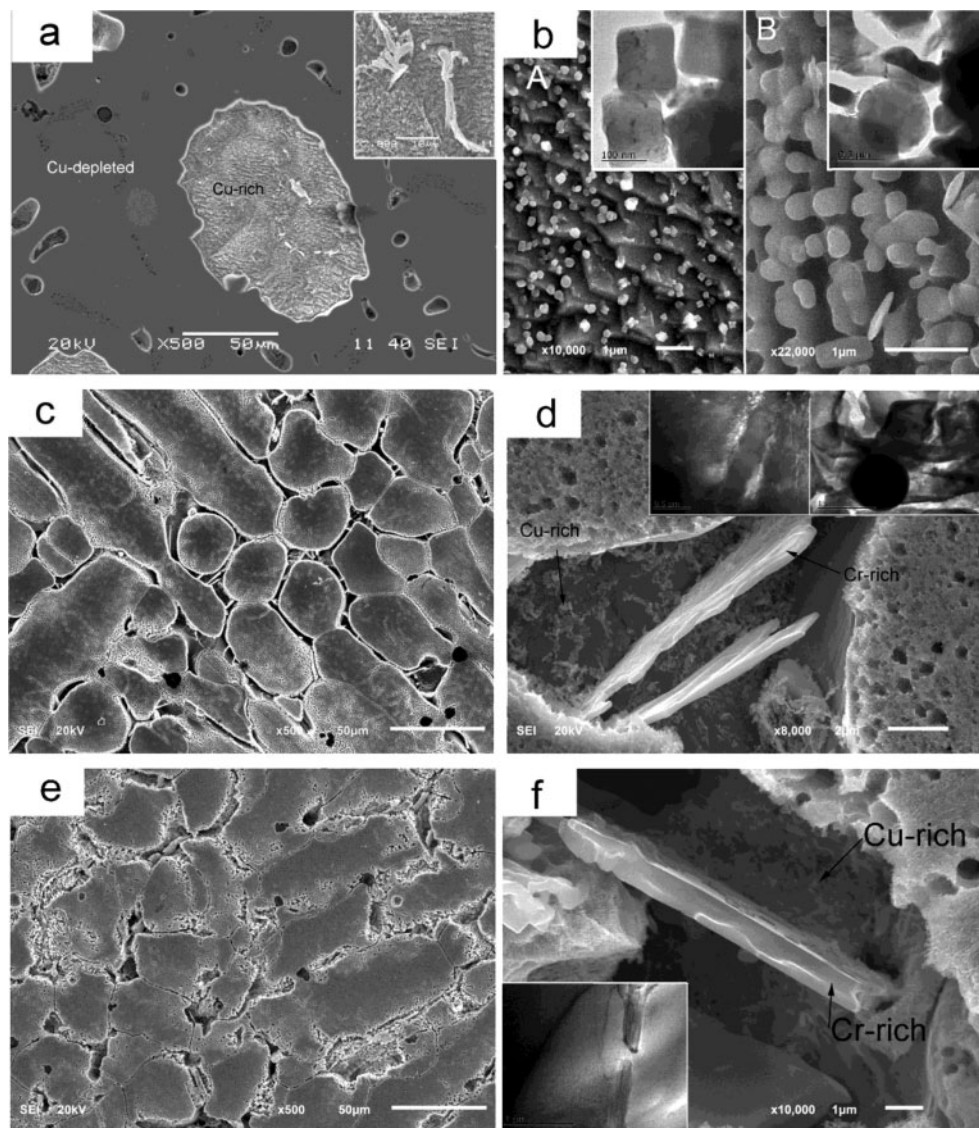
(EDS), and transmission electron microscope (TEM, JEM-2100F) and performed using thin foil specimens prepared by mechanical thinning and subsequent twin jet electrochemical polishing (8 vol.-% HClO_4 –92 vol.-% ethanol solution) and ion milling.

Results and discussion

Cu rich spheric structures are observed in the microstructure of $\text{CoCrCuFe}_{0.5}\text{Ni}$ alloy (Fig. 1a), which indicates that liquid phase separation had occurred in the initial liquid before the occurrence of liquid solid transformation. During liquid phase separation, the decomposition of the initially homogeneous liquid starts with nucleation of the liquid minority phase in the form of droplet to reduce the interface energy between the two liquids¹¹ In the $\text{CoCrCuFe}_{0.5}\text{Ni}$ alloy, the liquid minority phase is the Cu rich liquid, and many Cu rich droplets form in the initial liquid before the liquid–solid transformation. Relatively, the liquid around the Cu rich droplets is the Cu depleted liquid, which solidifies to form typical dendritic (rich in Co, Cr and Fe elements) and interdendritic structures (rich in Cu and Ni elements), as

shown in Fig. 1a. It is noted that nanoprecipitates with various morphologies are found in the interdendritic regions. In region A (Fig. 1b, A), many spherical structures (230 nm in diameter) can be seen in the step-like matrix, while in region B (Fig. 1b, B), many chip-like structures (726 nm in length and 134 nm in width) can be observed. The former is detected to be abundant in Cu element, and the latter is rich in Cr element. The further result is confirmed by TEM bright field, as shown in the inserted graph of Fig. 1b (A and B).

Cu rich spheric structures cannot be found, but typical dendrites are obtained in the microstructure of $\text{CoCrCuFe}_x\text{Ni}$ ($x \geq 1.0$) alloys, as shown in Fig. 1c, e and g. It means that liquid phase separation had not occurred in $\text{CoCrCuFe}_x\text{Ni}$ ($x \geq 1.0$) alloys before solidification. Substructures are found in the dendrites of equiatomic CoCrCuFeNi high entropy alloy, and TEM bright field image shows the detail in Fig. 1c. As shown in Fig. 1d, rod-like structures can be observed in the interdendritic region of CoCrCuFeNi alloy. At the same time, little granules are found at the dendrite boundary (Fig. 1d). The EDS analysis demonstrates that Co, Cr, Ni and Fe elements are rich in the dendrites, while the



a, b $x = 0.5$; c, d $x = 1.5$; e, f $x = 2.0$

2 Microstructures and nanostructures of CoCrCuFeNi_x high entropy alloys

content of Cu element is obviously higher in the interdendritic region. Additionally, the granules at the dendrite boundary are rich in Cr element, TEM bright field image of which is inserted in Fig. 1d.

Many Cr rich needle shaped structures can be seen at the grain boundary of the dendrites in the microstructure of CoCrCuFe_{1.5}Ni alloy, as shown in Fig. 1e. Figure 1f shows Cu rich rhombus precipitates (481 nm in length and 128 nm in width) in the interdendritic region, which is confirmed by TEM bright field. Similarly, cubic-like precipitates (215 nm in size) are observed in the interdendritic region when $x = 2.0$ (Fig. 1h). It is worth noting that a uniform nanoscale cellular structure precipitates in the dendritic region of CoCrCuFe_{1.5}Ni high entropy alloy, as inserted in Fig. 1e.

Similarly, liquid phase separation occurs and spheric structures are observed in the CoCrCuFeNi_{0.5} alloy. The microstructure consists of two different regions: the Cu rich spheres and Cu depleted regions. More Cu rich spheric structures can be seen, and some of them get together with each other and show ellipse shape (Fig. 2a). In the Cu rich spheres, some Cr rich bird-like structures can be found, as shown in the inserted graph in Fig. 2a. Furthermore, Cu rich nanoparticles (Fig. 2b, A) and Cr rich flake-like structures (Fig. 2b, B) can be observed in the spheres. TEM bright field images of the precipitates are inserted in Fig. 2b. Conversely, typical dendritic and interdendritic structures can be seen in the Cu depleted region. The volume fraction of the interdendritic region and the size of nanoprecipitates decrease with the increase of the molar ratio of Ni element. At the same time, large block of lath shaped Cr rich structures can be seen in the interdendritic region of CoCrCuFeNi_{1.5} and CoCrCuFeNi_{2.0} alloys (Fig. 2c–f). In the inserted graph, TEM bright field images of Cr rich structures and nanoprecipitates can be seen in Fig. 2.

According to Takeuchi and Inoue,¹⁶ the enthalpies of mixing between Co, Cr, Fe, Ni and Cu are +6, +12, +13 and +4 kJ mol⁻¹ respectively. So Cu cannot mix with other elements thermodynamically, and the weak mutual solubility between Cu and the other elements results in the segregation of Cu rich phase in the microstructure. The molar mixing entropy ΔH is related to the constant $\Delta H_0 = 4\Delta H_{AB}^{\text{mix}}$, which is connected with the interatomic interactions between the A and B atoms. According to Ratke and Diefenbach,¹¹ depending on whether the interatomic energies in the alloy are stronger or weaker than in the unmixed components at the given molar fraction x , there is a tendency towards compound formation (preferred neighbourhood of different atoms) or towards phase separation (preferred neighbourhood of the same atoms). Generally, immiscible alloys are characterised by a positive value of ΔH_0 . The mixing enthalpies of CoCrCuFe_{0.5}Ni and CoCrCuFeNi_{0.5} alloy are calculated to be +3.06 and +4.44 kJ mol⁻¹ respectively. The positive mixing enthalpies of the alloys can be reasons for liquid phase separation.

Including five or more constituents, diffusion in multicomponent high entropy alloy is much slower than conventional alloys. Moreover, the atomic radii of the component elements in CoCrCuFeNi alloys are 0.125, 0.128, 0.128, 0.127 and 0.125 nm respectively.¹⁶ The small difference of atomic radius for CoCrCuFeNi

alloys leads to sluggish cooperative diffusion of the component elements and consequently causes the formation of supersaturated solid solution. As a result, nanoscaled phases precipitate in the microstructure during the cooling process.

Conclusions

In summary, the as solidified microstructures of CoCrCuFe_xNi and CoCrCuFeNi_x ($x = 0.5, 1.0, 1.5$ and 2.0) high entropy alloys have been studied in this present work, with a particular attention to the liquid phase separation of CoCrCuFe_{0.5}Ni and CoCrCuFeNi_{0.5} alloys. Spherical structures were observed in the microstructure of CoCrCuFe_{0.5}Ni and CoCrCuFeNi_{0.5} alloys, which were generated from the nucleation of the Cu rich liquid phase in the initially homogeneous liquid. Dendritic and interdendritic structures were obtained in the microstructures of CoCrCuFeNi_x and CoCrCuFe_xNi ($x = 1.0, 1.5$ and 2.0) high entropy alloys. Especially, Cu and/or Cr rich precipitates, with different morphologies, were observed in the interdendritic region, as well as in the liquid phase separated Cu rich spheres. The small difference of atomic radius for CoCrCuFeNi alloys causes sluggish cooperative diffusion of the component elements, which result in segregation and formation of nanoprecipitates in the microstructure. The positive mixing enthalpies of CoCrCuFe_{0.5}Ni and CoCrCuFeNi_{0.5} alloys are likely reasons for liquid phase separation.

Acknowledgements

The authors are grateful to the financial support of the National Natural Science Foundation of China (grant nos. 51201072 and 51471079) and Qinglan Project of Jiangsu Province. P. Wu is grateful to the financial support of Graduate Student Innovation Projects of Jiangsu University of Science and Technology (grant no. YSJ14S-15) and Graduate Student Innovation Projects of Jiangsu Province (grant no. SJLX15-0530). This work is supported by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

1. J. W. Yeh, S. K. Chen and S. J. Lin: 'Nanostructured high-entropy alloys with multiple principal elements: novel alloy design concepts and outcomes', *Adv. Eng. Mater.*, 2004, **299**, 6–12.
2. B. Cantor, I. T. Chang and P. Knight: 'Microstructural development in equiatomic multicomponent alloys', *Mater. Sci. Eng. A*, 2004, **A375–A377**, 213–218.
3. Z. Wu, H. Bei, F. Otto, G. M. Pharr and E. P. George: 'Recovery, recrystallization, grain growth and phase stability of a family of FCC-structured multi-component equiatomic solid solution alloys', *Intermetallics*, 2014, **46**, 131–140.
4. Z. Wu, H. Bei, G. M. Pharr and E. P. George: *Acta Mater.*, 2014, **81**, 428–441.
5. Z. Wu and H. Bei: 'Microstructures and mechanical properties of compositionally complex Co-free FeNiMnCr18 FCC solid solution alloy', *Mater. Sci. Eng. A*, 2015, **A640**, 217–224.
6. T. T. Shun and Y. C. Du: 'Microstructure and tensile behaviors of FCC Al_{0.3}CoCrCuFeNi high entropy alloy', *J. Alloys Compd.*, 2009, **479**, 157–160.
7. C. J. Tong, Y. L. Chen and M. R. Chen: 'Microstructure characterization of Al_xCoCrCuFeNi high-entropy alloy system with multiprincipal elements', *Metall. Mater. Trans. A*, 2005, **36**, 881–889.

8. S. Guo, C. Ng and C. T. Liu: 'Sunflower-like solidification microstructure in a near-eutectic high-entropy alloy', *Mater. Res. Lett.*, 2013, **4**, 228–232.
9. C. J. Tong, M. R. Chen and S. K. Chen: 'Mechanical performance of the $\text{Al}_x\text{CoCrCuFeNi}$ high-entropy alloy system with multiprincipal elements', *Metall. Mater. Trans. A*, 2005, **36**, 1263–1271.
10. Z. Y. Liu, S. Guo, X. J. Liu, J. C. Ye, Y. Yang, X. L. Wang, L. Yang, K. An, and C. T. Liu: 'Micromechanical characterization of casting-induced inhomogeneity in an $\text{Al}_{0.8}\text{CoCrCuFeNi}$ high-entropy alloy', *Scr. Mater.*, 2011, **64**, 868–871.
11. L. Ratke and S. Diefenbach: 'Liquid immiscible alloys', *Mater. Sci. Eng. R*, 1995, **R15**, 263–347.
12. 'ASM metals handbook', 1992, Metals Park, OH, ASM International.
13. P. H. Wu, N. Liu, W. Yang, Z. X. Zhu, Y. P. Lu and X. J. Wang: 'Microstructure and solidification behavior of multicomponent CoCrCuFeMoNi high-entropy alloys', *Mater. Sci. Eng. A*, 2015, **642**, 142–149.
14. C. M. Liu, H. L. Tsai and H. Y. Bor: 'Effect of aging treatment on microstructure and properties of high-entropy $\text{Cu}_{0.5}\text{CoCrFeNi}$ alloy', *Intermetallics*, 2010, **18**, 1244–1250.
15. C. M. Liu and H. L. Tsai: 'Effect of annealing treatment on microstructure and properties of high-entropy $\text{FeCoNiCrCu}_{0.5}$ alloy', *Mater. Chem. Phys.*, 2011, **128**, 50–56.
16. A. Takeuchi and A. Inoue: 'Calculations of amorphous-forming composition range for ternary alloy systems and analyses of stabilization of amorphous phase and amorphous-forming ability', *Mater. Trans. JIM*, 2001, **42**, 1435–1444.